

Transport of iodine and mercury contained in submicronic aerosol particles over relatively clean seas (the Antarctic) and polluted ones (the Baltic)*

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Aerosol particles
Iodine
Mercury
Admiralty Bay
Spitsbergen
Gulf of Gdańsk

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Abstract

The sea-air exchange of iodine and mercury contained in aerosol was studied with consideration to the submicronic particle size distributions. The method applied was the analysis of reactive traces using the electron microscopy technique.

1. Introduction

Blanchard and Woodcock [3] elucidated the importance of the mechanism of gas bubbles bursting in the particle injection from the sea surface into the atmosphere. Next, MacIntyre [9] calculated that the bubble outer envelope, its thickness being 0.05‰ of its diameter, becomes during its bursting the source of substances contained in the first jet drop, and the following layer 0.5 μm thick forms the next drop, etc. Thus, the chemical constitution of the drop will be determined mainly by the chemical constitution of the bubble surface. On the other hand, it is natural to assume that the contribution of microelements accumulated in the sea surface film should dominate mainly in the sets of drops of film origin. Together with this, the evolution of the sea surface film chemical constitution should proceed under the influence of direct aerosol capture on the sea surface as well as of evaporation and precipitation. One cannot rule out probable influence of diffusion of substances dissolved in water. The resulting fractionation effect, following the sea-to-air outflux of particles, causes that in the marine aerosol the concentrations of such metals

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as Cr, Cu, Fe, Hg, Pb and Zn are approximately four times higher than those in oceanic water [5, 6, 13, 14].

There is also a dependence of the fractionation effect on the aerosol particle sizes. Barker and Zeitlin [1] state that iodine concentration in the particles is inversely proportional to their sizes, and the bulk of such elements as Cu, Zn, As, Cd, Pb, Se, Ag is accumulated on the aerosol particles, their radii being less than 1 μm .

Taking the above into account, it can be assumed that diffusion transport of microelements to the sea surface and their outflux with water drops to the atmosphere can be investigated by means of some selected natural tracers. In the present paper, the particles of sea salt (NaCl) are taken as such tracers. Changes in the concentrations of I and Hg, if compared to that of Na in the sea-salt particles emitted to the atmosphere near the sea surface layer, enable the efficiency of pollution air-sea exchange to be studied. The efficiency of processes should depend on the level of pollution of a given air-water area and also in meteorological conditions.

2. Theory

It can be assumed that the average concentration of a given microelement connected with the marine aerosol is the sum of the following components:

$$\bar{q}mN = q_{n_f}mn_f + q_{n_j}mn_j + q_{n_c}mn_c, \quad (1)$$

where m — the particle mass, \bar{q} — the average contribution, and q_{n_f} , q_{n_j} , q_{n_c} — the individual contributions of the microelement in the sum, N — the total number of particles, *i.e.* the sum of the numbers of marine drops n_f and n_j — of film and jet origin, respectively, and n_c — the number of particles carried from above the land:

$$N = n_f + n_j + n_c. \quad (2)$$

The efficiency of the emission of particulate pollution transported from the sea, can be determined by the coefficients:

$$c_f = \frac{q_{n_f}}{q_f} \quad \text{and} \quad c_j = \frac{q_{n_j}}{q_w}, \quad (3)$$

where q_f and q_w — the relative contributions of the given microelement in the sea surface film mass and the sea subsurface layer mass, respectively. In the case of volatilization of the given component from the sea surface, it can be assumed that, additionally, the process of sorption of that gas by the aerosol particles suspended in the air takes place. Taking this process into account, one should also distinguish q_a — the contribution of the microelement volatile component. However, when $q_a \ll q_w \ll q_f$,

the contribution of q_a can be neglected.

Taking into account the simultaneous process of self-purification of the near-

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-water air layer over the sea by sedimentation of particles to the sea and their diffusion, accompanying turbulent air mixing, one can write the equation of the change in the number of particles dispersed in the air in the following form:

$$\Delta n = cn_0 \Delta t - \eta_s n \Delta t - \eta_D n \Delta t, \quad (5)$$

where n_0 — the number of the marine-aerosol particles originating from local particle emission and advection; η_s and η_D — the efficiencies of particle sedimentation and diffusion in the near-water air layer, respectively.

If sedimentation dominates over particle coagulation, then, after a time t_s greater particles in the suspended matter will decrease in favour of submicronic ones. In this connection, the fact that film drops are much smaller than the jet ones (typical radius $r_f \ll r_j$) gives rise to the conclusions regarding different contributions in a colloidal system of the particles responsible for the highest concentrations of the given microelement, also the contributions of diffusion and sedimentation conditions in the atmosphere. Besides, the influence of aerosols of non-marine origin should be of great importance, particularly in the case of higher concentrations of these particles, their radius being $r_c \lesssim r_f$, occurring mainly in coastal areas, most of all in the proximity of industrial centres. One may expect the occurrence of intensive coagulation of these particles with small film particles under such conditions, and hence an increase in the weight of sedimentation. The modifying effect of diffusion on the suspended matter evolution and on the decrease in the contribution in this matter of particles being the carriers of a microelement typical for the sea should be greater over water areas near the land than, for instance, over the open ocean. This is so because in the latter case, as well in the similar ones, local diffusion over the area which is in great part homogeneous cannot affect the anomalous deflection from the microstructure of the dispersed system in which the contribution n_f should be relatively great.

The purpose of the present paper is to study the contribution of the sea aerosol particles, in this film and jet drops, and also the particles of non-marine origin, on the iodine and mercury exchange processes between the sea and the atmosphere.

3. Method

3.1. Aerosol study

The samples of aerosols and the sea surface film were collected over the period from December 1978 to May 1979 in the open Baltic and the Gulf of Gdańsk regions. Simultaneously, similar samples were collected in the Admiralty Bay (the Antarctic)

and somewhat later on Spitzbergen (August, September 1980). This, in a way, had the weight of comparative studies of the expected natural background.

Aerosols were collected on fibrous filters type microsorb SM 15 903 of Sartorius production. In this order, a filtering device from the same firm was used and 300 m³ of air were pumped onto the sample. In the Baltic, the filtration was made on the upper deck of the R/V "Hydromet" (at a height of about 8 m above the sea surface). The filtration place was chosen as not to be near the ship's exhaust pipes. When the filters were exposed on the ship, air flowing from behind the board was pumped. Parallel to the measurements in the open gulf, the analogous filtration was made in Gdynia where the aerosols were collected on a tower at a height of 12 m above the sea surface and at a distance of about 50 m from the shore. At the stations in the polar regions, the filtering devices were exposed on a level of 2 m above the ground, 20 m from the sea shore. After the exposure, the filters were subjected to three-times repeated hot desorption (30 min. each) by means of spectrally pure nitric acid diluted with redistilled water in proportion 1 : 1. The total mercury content in a sample was determined by the atomic absorption method using the cold vapour technique. For the analysis, a monitor appropriated for mercury determination from the Laboratory Data Control (U.S.A.) was used. The determinability limit for mercury was 0.2 ng Hg.

For the micrometric analysis, the samples were collected on specially prepared microscopic nets used in electron microscopy. The aerosols were collected using a single-cascade impactor pumping some 100 m³ of air onto the sample. Dry fall-out was accumulated by exposing the nets for 50 hours on a jib located at a height of 3 m above sea level. It was endeavoured to collect each sample under similar atmospheric conditions, i.e. without fog and precipitation.

The particle size distribution and concentration of microelements in the aerosol were investigated using a transmission electron microscope TESLA 243 BS. The method employed was that of examining post-reactive traces of mercury-bearing and iodine-bearing particles with gold and silver placed on microscopic nets in the form of thin films. It was found that, in consequence of reactions of mercury-bearing particles (Phot. 2) and iodine-bearing particles with gold (Phot. 3), characteristic envelopes for the given element were formed around them. These traces could be easily identified using the transmission electron microscope. The optimal gold- or silver-film thickness was 5 µm for the particles 1–2 µm in diameter. The smaller particles get stuck in the film, whereas the greater ones do not enable accurate quantitative estimation of the contents of the studied microelements on and/or in them. It was also found that when the metal-film thickness was kept constant, then the size of the post-reactive spot depended on the particle size and on the microelement concentration in it. The qualitative and quantitative settlements regarding method of this type, known from the bibliography [2], concern sulphur and halogens. For this study, laboratory tests with artificially-produced particles were made. Owing to them, it was found that the method applied enabled to study on this ground qualitative and quantitative contributions of natural mercury-bearing (Phot. 1) and iodine-bearing (Phot. 4) particles in sea aerosols and to distinguish these particles

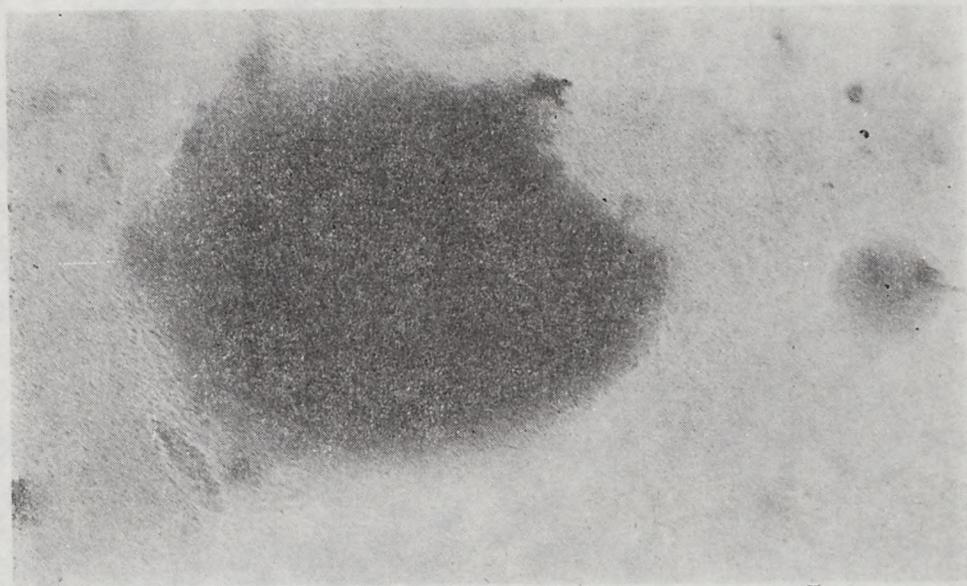


Photo 1. Microphotograph of artificially prepared mercury-bearing particle with reaction traces on a gold film $50 \cdot 10^{-3}$ μm thick ($\times 4600$)

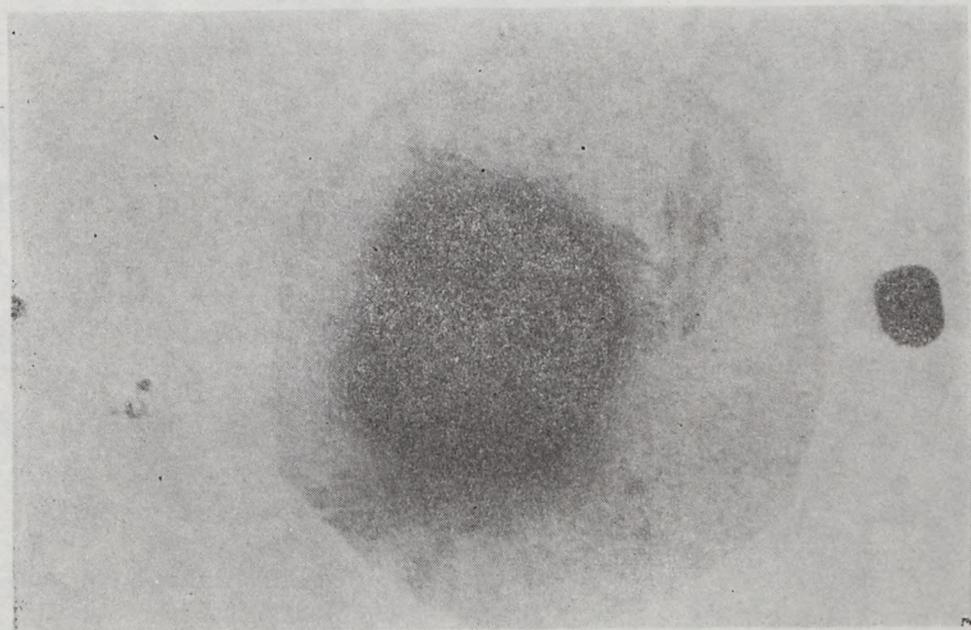


Photo 2. Microphotograph of mercury bearing particles of the Baltic aerosol with reaction traces on a gold film $50 \cdot 10^{-3}$ μm thick ($\times 4600$)

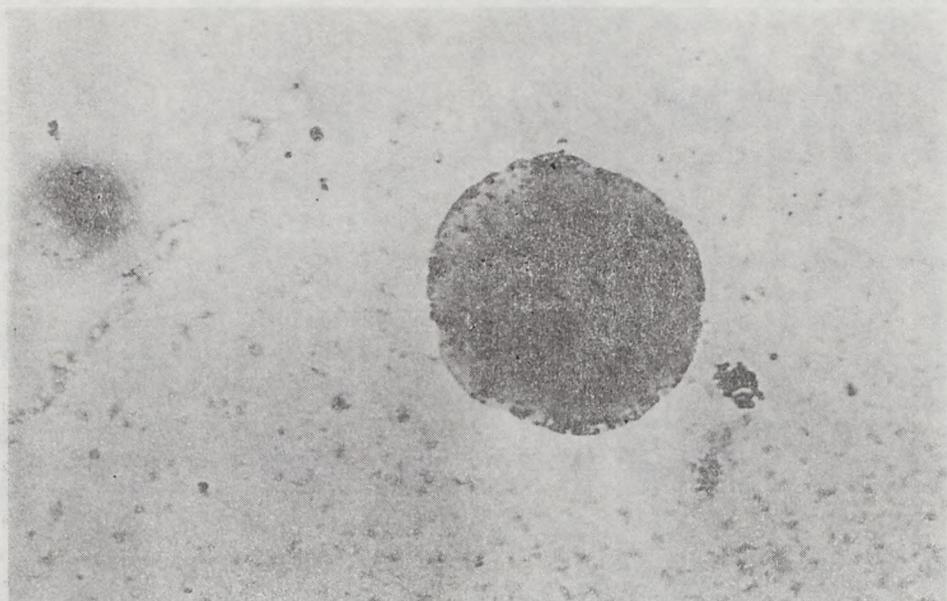


Photo 3. Microphotograph of natural iodine-bearing particles with reaction traces on a gold film $50 \cdot 10^{-3} \mu\text{m}$ thick ($\times 4600$)

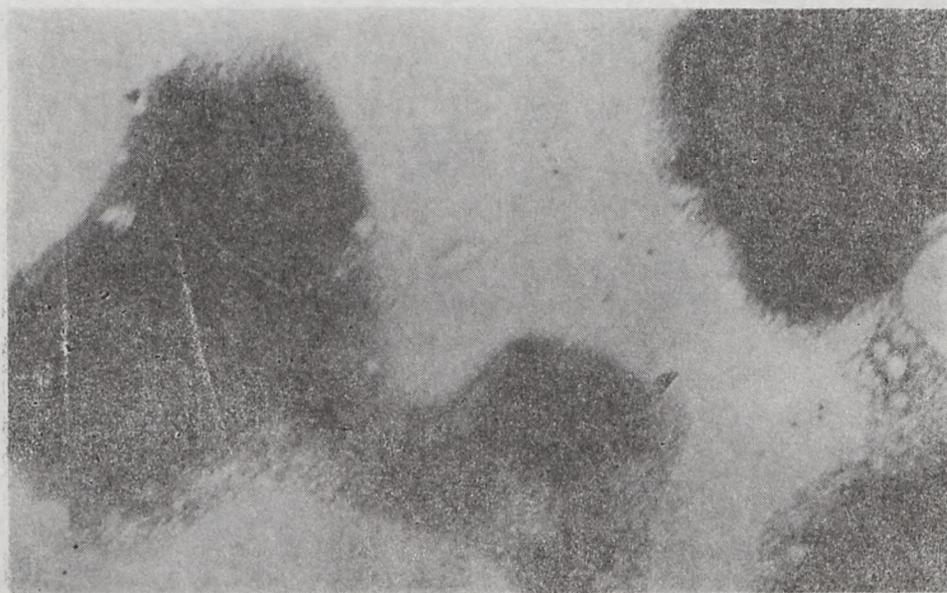


Photo 4. Microphotograph of artificial iodine-bearing particles with reaction traces on a gold film $50 \cdot 10^{-3} \mu\text{m}$ thick ($\times 4600$)

from those making no traces characteristic for iodine or mercury reactions with gold or silver. It can be assumed that a number of the latter particles, even containing the above microelements, can be non-detectable as regards the microelement-content on and/or in them.

3.2. Mercury measurements in the sea surface film

Additionally, the sea surface film was sampled and in this order glass plates (40×40 cm) were used. The plate was immersed in the sea perpendicularly to the sea surface and, after pulling it out, the surface film sample, adhering bilaterally to the plate, was scraped off with a teflon knife. The sample was collected in a polyethylene vessel. In order to protect the sample from losing mercury, concentrated spectrally pure nitric acid was added to it. The mercury total content in the sample, after its cold mineralization with potassium permanganate and sodium persulphate, was determined employing the atomic absorption method. Simultaneously, the sea near-surface layer was sampled by bathometers. The water samples were, in practice, taken only from the layer of down to the depth of ≈ 0.5 m. Before the collected water was analysed, it had been stored under the same conditions as the sea surface film samples. The total mercury content in the samples was also determined by means of the atomic absorption method.

4. Results and discussion

Employing the air filtration method, it was generally found that the mercury total concentration in atmospheric aerosols (Table 1) over the Baltic was 6 times as large of those over the Admiralty Bay and Spitsbergen regions. It is, therefore, clear that the polar regions are relatively clean areas whereas the Baltic Sea is an extremely polluted sea. This fact is revealed especially by the data regarding the mercury content in the sea surface film (Table 2). In this case, the differences between various regions are of one order of magnitude. This is caused by the conditions of considerable mercury accumulation in the sea surface film, since the concentration of this microelement is on the average by two orders of magnitude higher here than in the near-surface sea layer. It seems interesting that this relation is approximately the same in the Baltic and in the polar regions (the Arctic, the Antarctic).

Basing on the considerably higher mercury concentrations measured in the air in the coastal zone, the atmosphere cannot be considered to be the main source of water pollution in such water areas as, for instance, the Gulf of Gdańsk. It is obvious that the mercury-polluted gulf can also be a source of secondary pollution of ambient air.

In order that the resultant direction of the pollution transport through the air-sea interface be determined, an attempt was made to find the contribution of mercury-bearing particles in the aerosols and the mercury content in the sea surface film.

Table 1. Total particulate mercury concentration in the near-water air layer

Region	Date of sampling	Average concentration (ng/m ³)
Baltic Sea	January'79	7.5
	February'79	7.0
	March'79	8.2
Gulf of Gdańsk	January'79	25.2
	February'79	38.7
	March'79	20.0
Gdynia	January'79	42.2
	February'79	50.8
	March'79	24.4
The Antarctic:		
Admiralty Bay	December'78	2.1
	January'79	3.3
The Arctic:		
Hornsund Fiord	July'80	1.3
	August'80	1.6

Table 2. Indicator of the mercury pollution level (I_{Hg} -ratio of the mean mercury concentration in the region considered to be the expected natural background measured in the polar regions) and the enrichment factor (E_{Hg}) of the sea-surface film in various regions

Region	Period	I_{Hg}	$E_{Hg} = \frac{q_f}{q_w}$
Arctic:			
Hornsund Fiord	July-August 1980	1.0	72-108
Antarctic:			
central area of the Ezcurra Inlet	February 1979	1.0	135
Coastal Station		1.0	51
Baltic Sea	January 1979 -		
	- March 1980	3.0-11.2	52-128
Gulf of Gdańsk	January 1979 -		
	- March 1980	4.8-13.3	64-142

The micrometric method employed in this study, together with the examination of reactive traces, enabled the particles forming a complex microstructure of marine aerosol collections to be classified in respect of iodine and mercury total contents on and/or in them. By that means, an attempt was also made to estimate the numbers of mercury-bearing and iodine-bearing particles carried from the sea to the atmosphere and in the opposite direction. That estimation was based on the morphometric analysis of aerosol particles, taking into account the particles their shape being characteristic of sea-salt (NaCl) nuclei.

From the analysis of relatively pure aerosol particles of marine and non-marine origin (Figs. 1, 2) and mercury-polluted sea-salt nuclei, it was found that the sea surface film is not only an excellent pollution sorbent (Table 2), but also participates in its transport to the atmosphere. Together with that, the results were obtained, manifesting that, on the average, among the sea-salt particles investigated in the

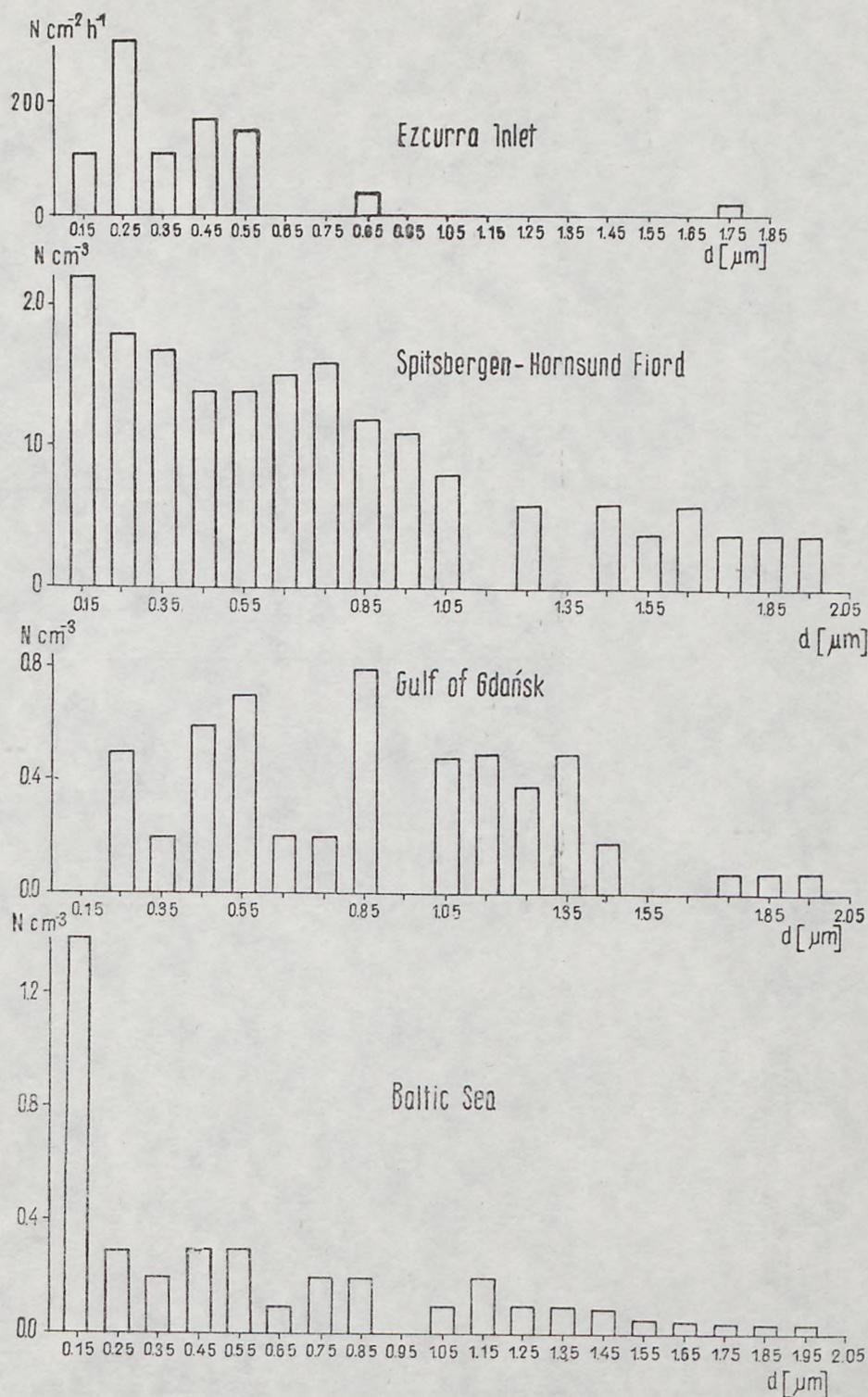


Fig. 1. Distribution of the number (N) of sea-salt particles with non-detectable mercury and iodine traces (based on 85 samples examined for the Gulf of Gdańsk and Baltic Sea regions, 50 samples — for the Ezcurre Inlet and 40 samples — for Spitsbergen, Hornsund Fiord)

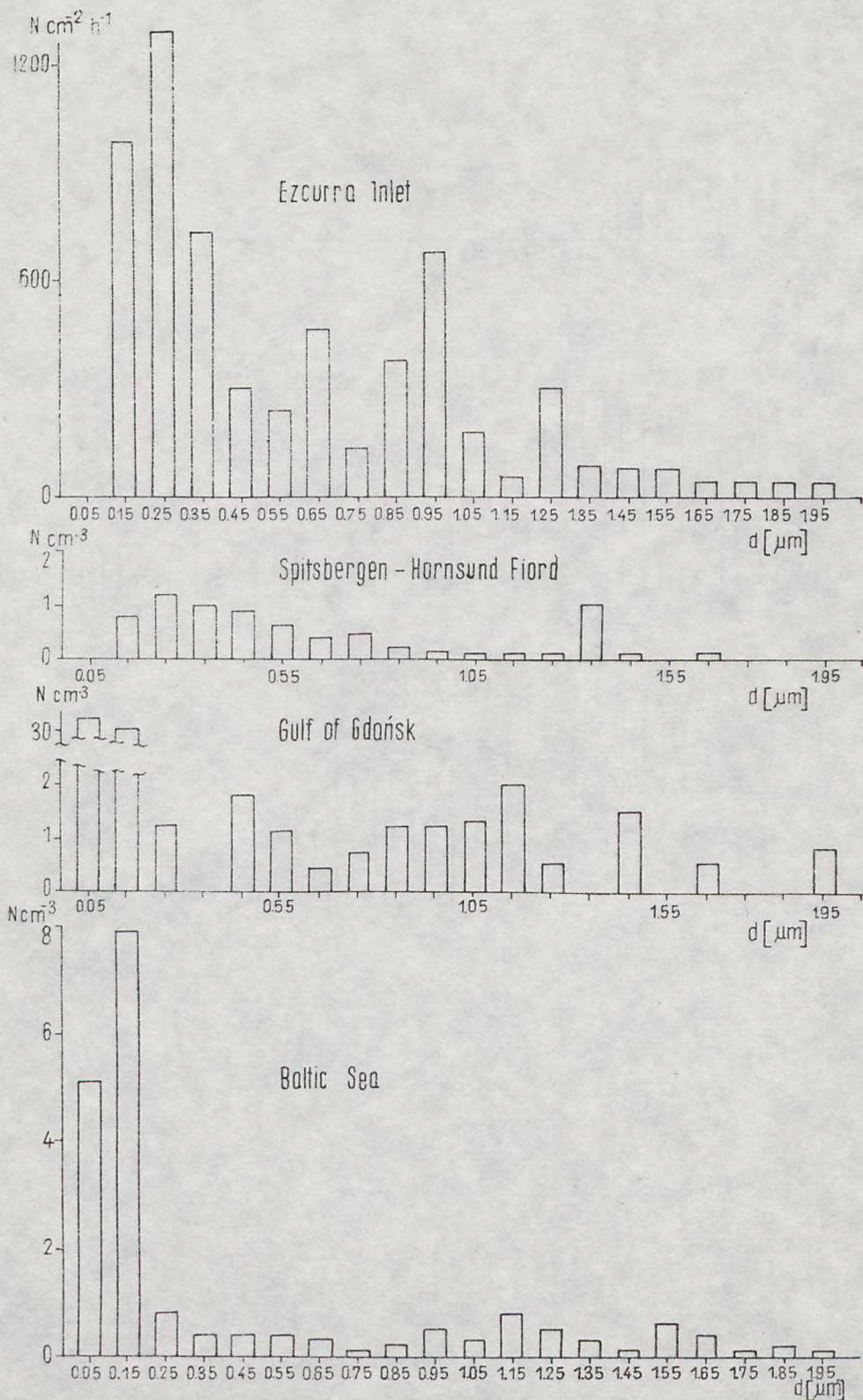


Fig. 2. Distribution of the number (N) of particles of non-marine origin with non-detectable mercury and iodine traces (based on 85 samples examined for the Gulf of Gdańsk and Baltic Sea regions, 50 samples — for the Ezcurra Inlet and 40 samples — for Spitsbergen, Hornsund Fjord)

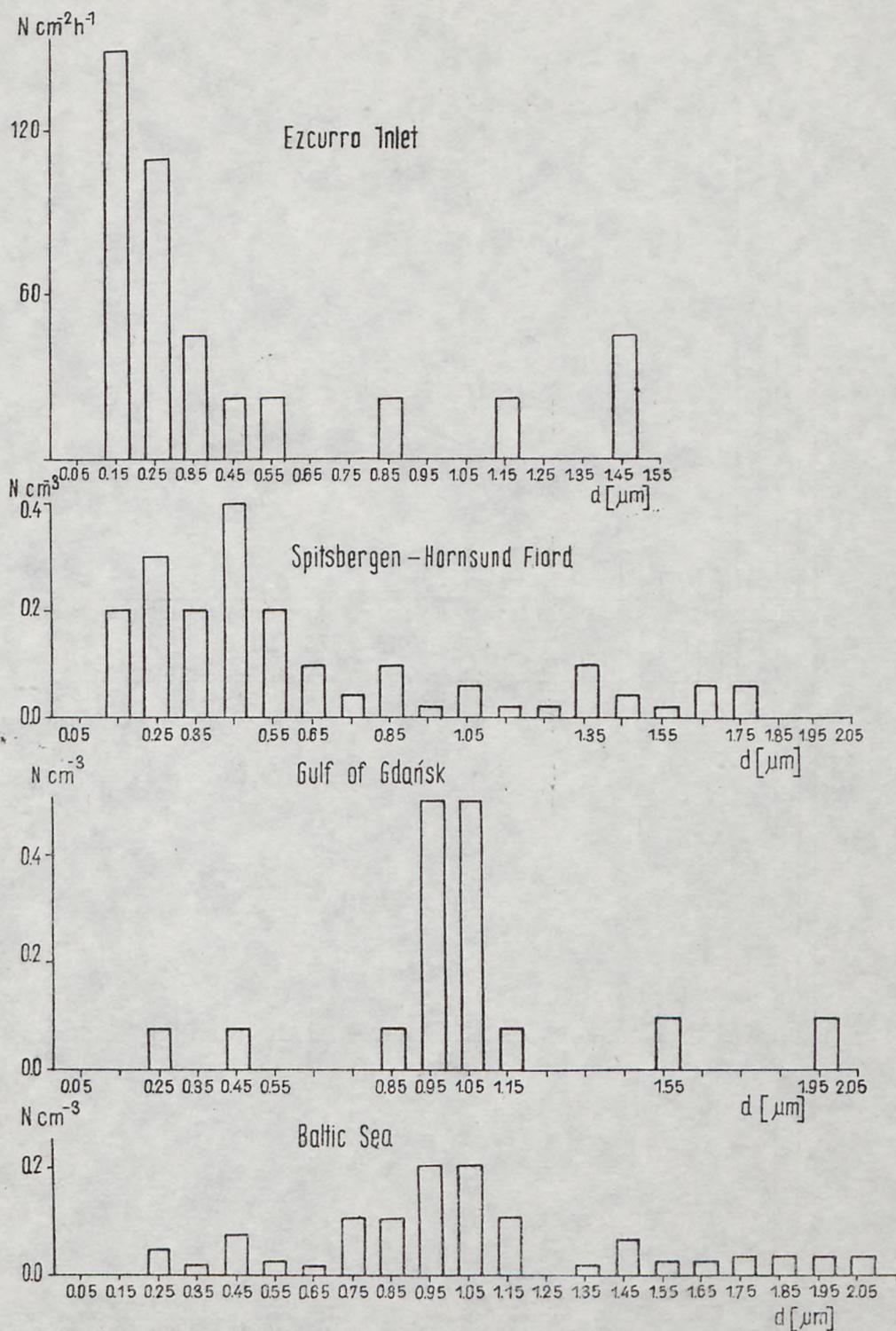


Fig. 3. Distribution of the number (N) of sea-salt particles with detectable mercury traces (based on 85 samples examined for the Gulf of Gdańsk and Baltic Sea regions, 50 samples — for the Ezcurre Inlet and 40 samples — for Spitsbergen, Hornsund Fiord)

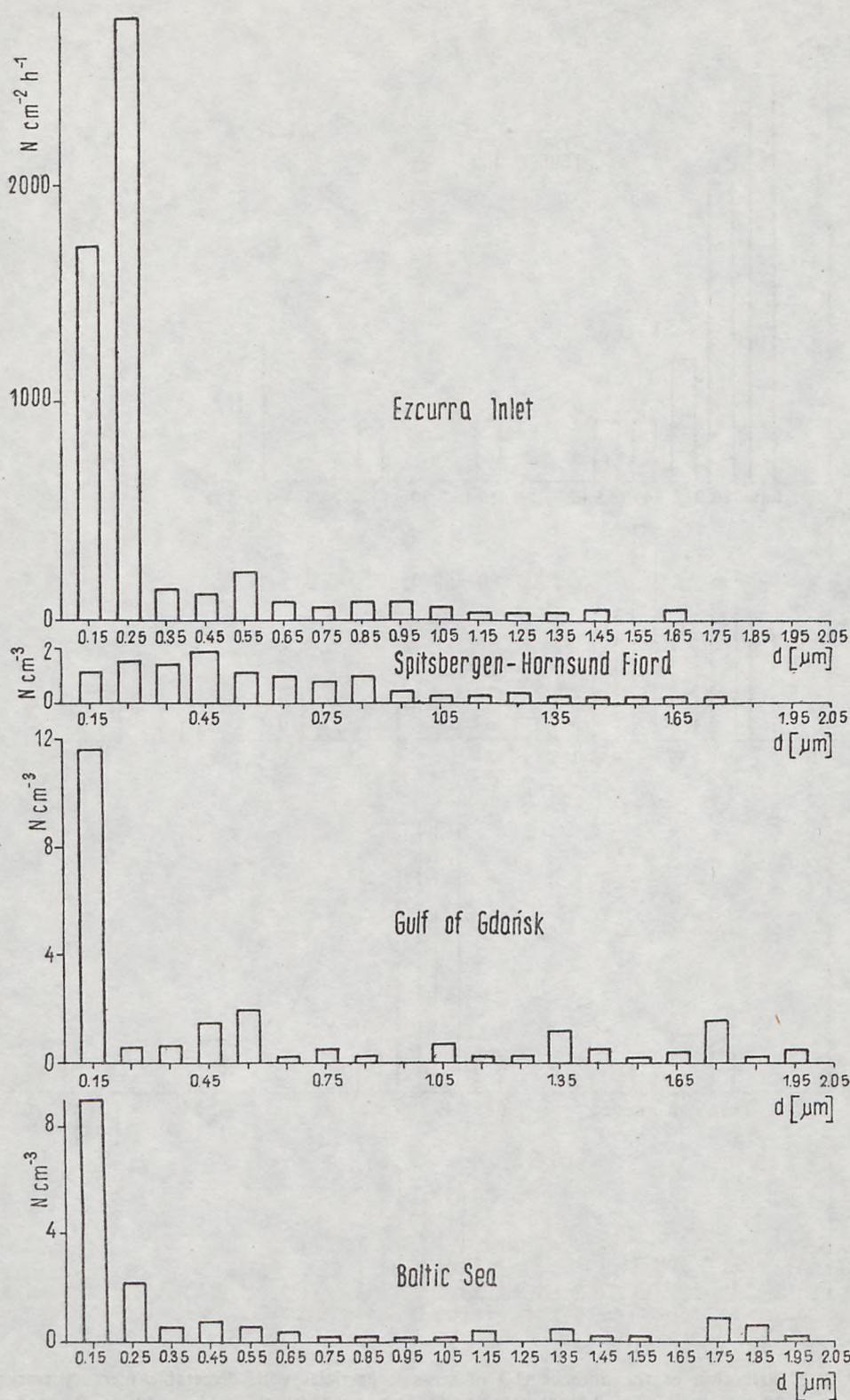


Fig. 4. Distribution of the number (N) of particles of non-marine origin with detectable mercury traces (based on 85 samples examined for the Gulf of Gdańsk and Baltic Sea regions, 50 samples – for the Ezcurre Inlet and 40 samples – for Spitsbergen, Hornsund Fiord)

Baltic and Gulf of Gdańsk regions the most effective mercury-carriers from the sea to the atmosphere are the particles 0.7–1.3 μm in diameter (Fig. 3). A relatively great contribution of the particles, their diameters exceeding 1.3 μm , in the mercury transport from the sea to the atmosphere can also be noticed, especially over the Baltic. It was also found that in the Baltic very intensive transport from the sea of mercury-bearing particles takes place, although in the area of the Gulf of Gdańsk a considerably greater number of such particles is observed. On the other hand, it seems that in the Antarctic and Spitsbergen regions (Fig. 3) the relatively smaller particles, 0.2–0.3 μm in diameter, are of the greatest importance in the mercury transport to the atmosphere.

The results of the investigations of the air-to-sea particulate mercury transport indicate that both in the Baltic, thereby in the Gulf of Gdańsk, and in the polar regions, first and foremost, submicronic particles 0.2–0.4 μm in diameter participate in this process (Fig. 4).

From the analysis of the aerosol samples, it follows that in the regions considered the drops ejected from the sea and their derivatives in the form of sea-salt particles also participate in the sea-to-air transport of iodine. It seems that the iodine contribution in the sea-aerosol particles is much greater in the polar regions (summer) than in the Baltic, especially in the Gulf of Gdańsk. This could evidence the intensive sea-to-air particulate iodine transport in the polar regions, which is likely to be connected with better oxygenation of sea water in these regions as well as with higher salinity.

In the sea-to-air transport of iodine on the sea-salt particles in the polar regions as well as in the Baltic region, mainly submicronic particles 0.2–1.4 μm in diameter take part (Fig. 5). This could testify to the influence of the organic sea-surface film constitution on the particulate iodine transport owing to the film-drop production. Thus, from the micrometric quantitative analysis of iodine-bearing particles, it follows that the iodine content in them increases with their diminishing sizes (Fig. 5). This statement is in accordance with Moyers and Duce's results [12] regarding the iodine concentration dependence on particle sizes.

Free iodine, liberated in the near-surface sea layer can also be evaporated to the atmosphere in the gaseous form. Its sorption by the particles suspended in the near-water air is probably another reason for aerosol enrichment with iodine, and is likely to act in the way similar to free iodine sorption on the sea surface. It was found, however, that the frequency of the occurrence of iodine-containing particles of non-marine origin (Fig. 6) was much lower than that of the particles of marine origin. Therefore, taking into account that the iodine transport from the sea occurs also with sea-water drops, it can be supposed that, in general, the iodine sea-to-air outflux dominates over that of the iodine air-to-sea input.

When studying the emission of the above-mentioned microelements, depending on the wind speed, it can be stated that for marine iodine-bearing particles a tendency to decrease their volume concentration with the increasing wind speed is observed in the range of $u_{10} \leq 4 \text{ m}\cdot\text{s}^{-1}$, and the opposite tendency is observable for the wind speed exceeding $4 \text{ m}\cdot\text{s}^{-1}$ (Fig. 8). In this respect, this dependence

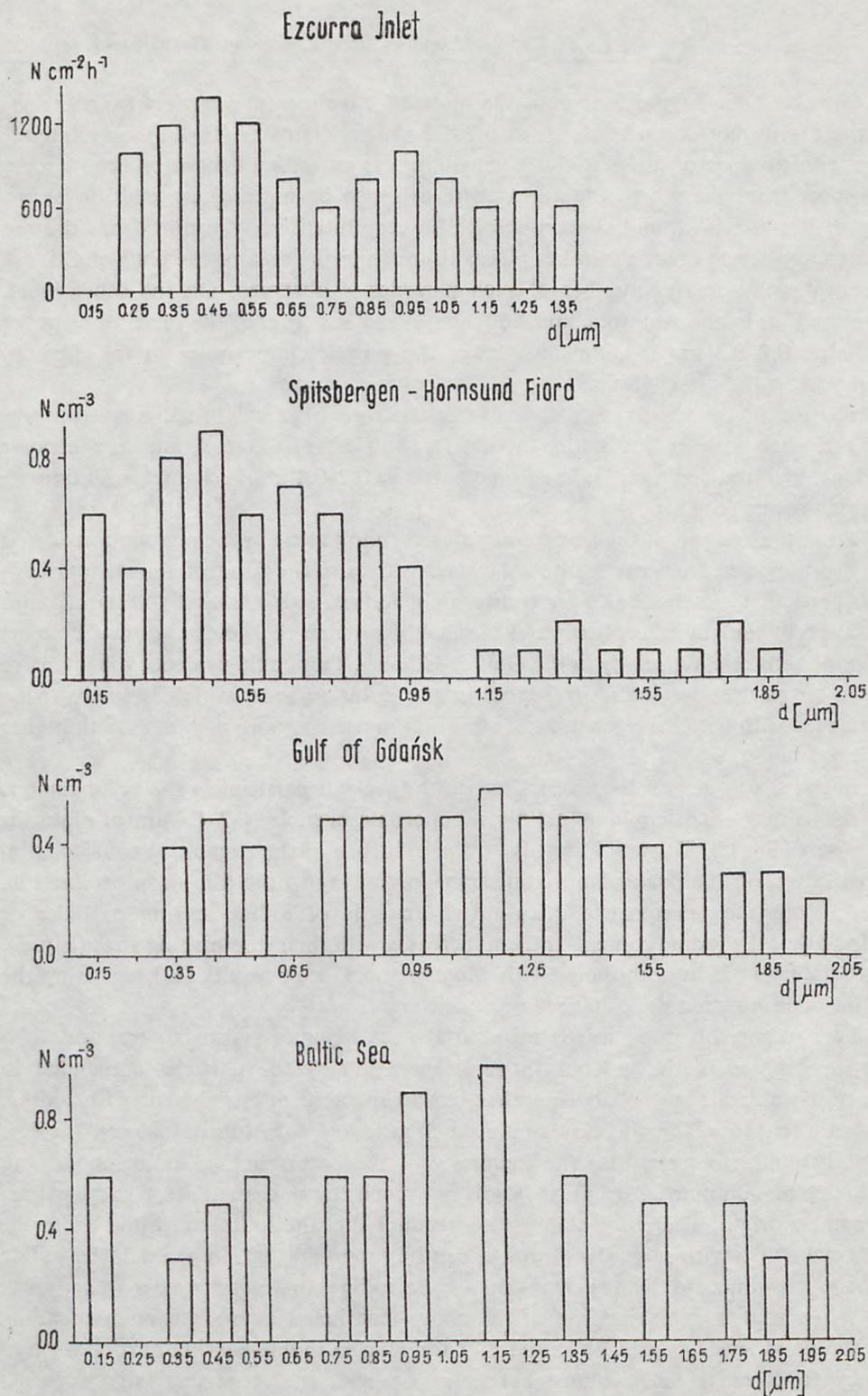


Fig. 5. Distribution of the number (N) of sea-salt particles with detectable iodine traces (based on 85 samples examined for the Gulf of Gdańsk and Baltic Sea regions, 50 samples — for the Ezcurre and 50 samples — for Spitsbergen, Hornsund Fiord)

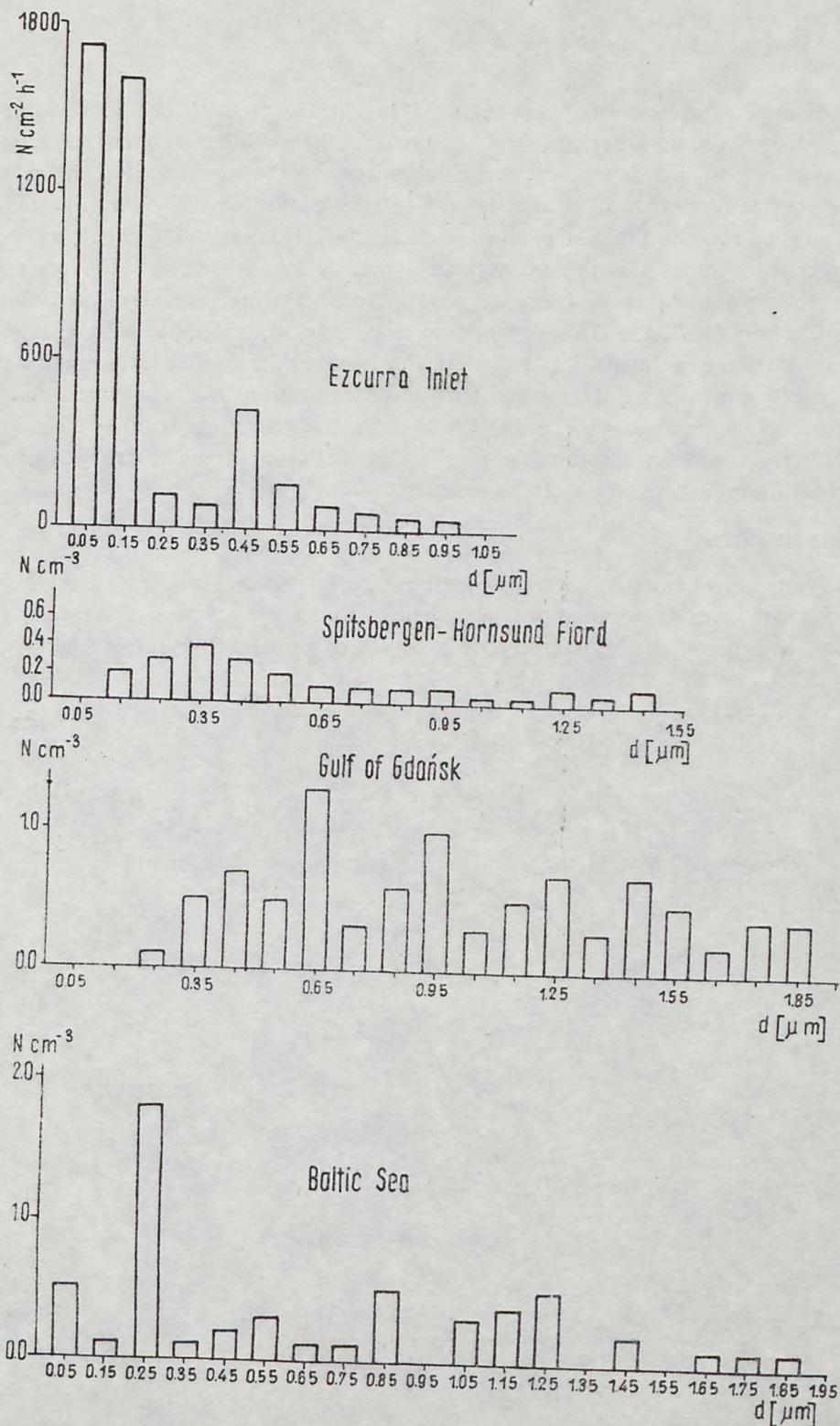


Fig. 6. Distribution of the number (N) of particles of non-marine origin with detectable iodine traces (based on 85 samples examined for the Gulf of Gdańsk and Baltic Sea regions, 50 samples — for the Ezcurre Inlet and 40 samples — for Spitsbergen, Hornsund Fiord)

differs from that for mercury of marine origin (Fig. 7). On the other hand, for iodine-bearing particles of non-marine origin, a decrease in their number with the increasing wind speed is observed. It seems that the dependence on the wind speed of the velocity of vertical exchange of microelements is affected by the diffusion-to-particle sedimentation ratio and the diffusion-to-particle production ratio. It can be assumed that specific properties of each element can also modify the dependence of the increase in the sea-salt particle emission on the wind speed, this being generally stated after several authors [4, 7, 15]. This dependence can, however, be additionally complicated by a change in the air-flow direction. For instance, in the Baltic, the influence of northerly winds upon the increase in the concentration of the marine iodine-bearing particles is observable on the one hand, and on the other hand — the effect of southerly winds on the increase in the concentration of the mercury-bearing particles of non-marine origin can be seen.

5. Conclusions

The method elaborated for investigating aerosol particles-iodine and mercury carriers, with consideration of marine particles and those of non-marine origin, enabled, together with the micrometric analyses of post-reactive traces employed

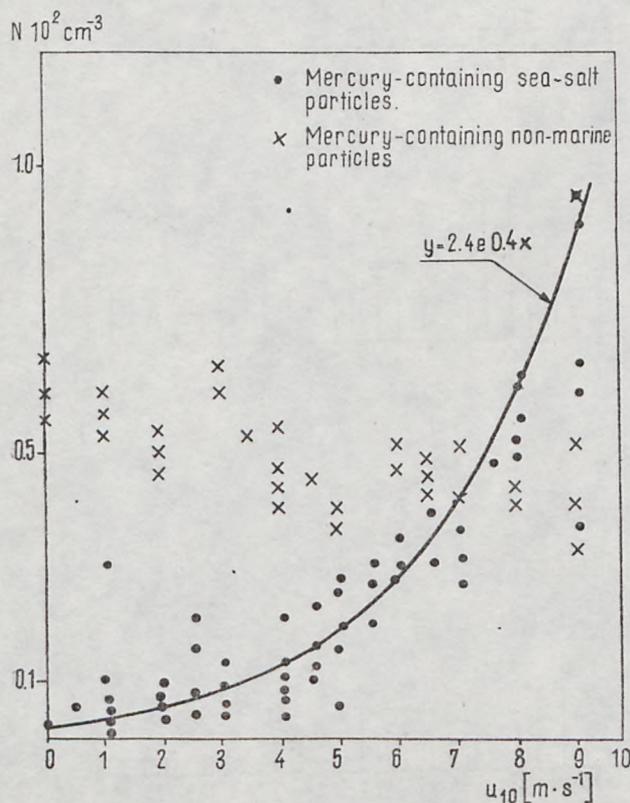


Fig. 7. Concentration dynamics of mercury-bearing particles in the near-water air over the open Baltic versus the wind speed. Data based on 85 aerosol samples examined

in it, to gain insight into some peculiarities concerning the mercury and iodine exchange between the sea and the atmosphere.

It was found that in the Baltic the particles approximately of $0.7\text{--}1.3\ \mu\text{m}$ in diameter are of great importance in the particulate mercury transport to the atmosphere, whereas the particles, their diameters being in the range of $0.1\text{--}0.4\ \mu\text{m}$, dominate in the air-to-sea transport of this microelement. In the Antarctic and Arctic waters, a shift in the size spectrum of the mercury-bearing particles transported from the sea is observed towards the smaller sizes as compared to those in the Baltic.

The sea-to-air iodine transport is more complex than that of mercury. Iodine-bearing particles are transported with marine drops, their derivatives – sea-salt particles being characterized by the diameters in the range of $0.1\text{--}1.4\ \mu\text{m}$ mainly. On the other hand, among the aerosol particles of non-marine origin, smaller particles ($0.1\text{--}0.4\ \mu\text{m}$) are mainly the iodine-bearing ones.

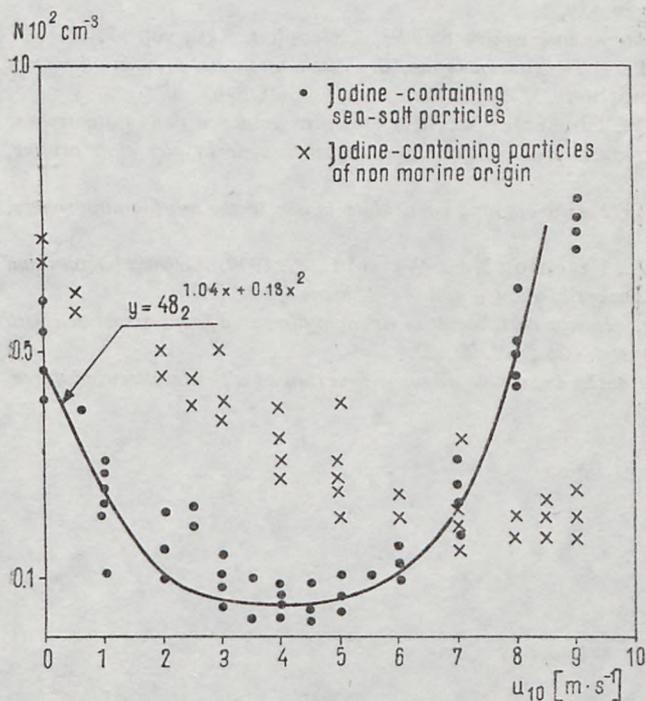


Fig. 8. Concentration dynamic of iodine-bearing particles of marine and non-marine origin in the near-water air over the Baltic versus the wind speed. Data based on 85 aerosol samples examined

Iodine enrichment of aerosols over the polar regions can easily be noticed, and the considerably weaker enrichment of aerosols over the open Baltic, especially over the area of the Gulf of Gdańsk, is very distinct. This fact is in conformity with the well-marked domination of the submicronic aerosol particles in the polar regions.

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